Petrochemical Opportunities in the New Nylons

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Nylon, the oldest wholly synthetic fiber type, continues to be in the major growth phase which has characterized its expansion over most of the last decade. World-wide consumption is expected to rise from 2.0 billion pounds in 1964 to at least 3.3 billion pounds by the end of the decade. Of the total world manufacturing capacity, estimated to reach 3.4 billion pounds/year by year-end 1966, some 40% is found in the United States, and 35% in Western Europe. Similarly, statistics place U.S. production at 45% of the 1964 total and Western Europe's share at 32%.

Significantly, world-wide growth is now proceeding at an accelerating rate, with the end of the uptrend not yet in sight. Following is the production performance during the period 1959–64:

	% Increase Over Previous Year Western Europe	Americas	All Other
1960	33	7	23
1961	15	17	22
1962	35	28	21
1963	25	14	33
1964	20	18	41
1959–64	175	114	242

Although the word "nylon" seems to conjure up the concept of sheer hosiery and apparel, above all, these constitute only about one-quarter of total nylon consumption. Instead, total U.S. demand in 1964 was distributed to the following estimated end use percentages:

Tires	32%
Carpets	22%
Hosiery and Socks	7%
Upholstery	6%
Apparel	17%
Industrial	9%
Stretch Fabrics	5%
Other	2%
	100%

The high growth rate in nylons (and other synthetic fibers) which characterizes the 1960's must be viewed as a long-awaited break-through in the highly conservative textile industry. In the industrial field, the progress has been made possible, above all, by better physical properties (e.g., tensile strength) than could be obtained at comparable cost in natural fibers. In the consumer field, the development has been tied to extensive consumer education, coupled with development of more widely acceptable after-processing techniques (dyeing to a large range of shades) and the introduction of products of special properties such as bulk and crimp development.

Even within the field of nylons, the difficulty of introducing a new fiber, or fiber type becomes apparent from experience with nylon-66 and nylon-6. The former appeared first on the American scene and, in 1964, accounted for 78% of nylon production* in the United States. In Germany, by contrast, nylon-6 was first available, and this type provided 65% of that country's nylon output during 1964.

There is not enough difference in the quality of these two nylon types to justify such sharp distinction in demand. Each has slight advantages and slight disadvantages over its competitive nylon type. Nylon-66 enjoys a somewhat higher softening point. Nylon-6, on the other hand, has the advantage of better weathering properties and, in some cases, better dye affinity. However, these distinctions are being blurred as new grades of each polyamide class become available. List prices for both types are the same (though nylon-6 has on many occasions been available in the U.S. at some discount below nylon-66).

Instead, the different degrees of acceptance for the various nylon types are grounded principally in historical priority. There are fine differences in dyeing and throwing characteristics, enough to make the fiber processor shy away from adapting his operations to a different fiber without obvious sharp advantage in price or properties.

Despite these customer attitudes which work against new fiber types, very considerable work is directed toward the development of new nylons. While there is always the hope for a lower-cost monomer or polymer at the end of the rainbow, there is now no development in sight which could hope to rival the general-purpose polyamides, i.e., nylon-6 or nylon-66.

Thus, the emphasis is on the development of nylon modifications or nylon types which will overcome a standard problem encountered with the established fibers—e.g., a fiber which avoids flat-spotting in tire cord, a product of higher softening point, a material of better electric properties (higher resistivity, lower moisture absorption), a nylon which can be crimped and bulked in the fabric, etc.

Many approaches may be taken in research toward these ends. The greatest publicity has been given to

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* The share of nylon-66 in fibers is even greater; in the U.S. nylon-6 finds substantially better acceptance in molded and extruded plastics than in fibers.

polyamides which differ in chemical structure from the standard nylons (such as nylon-7, nylon-11, etc.). Other techniques seek to achieve their objectives by physical modification of the base polymer, by some chemical modification (such as graft polymerization or cross-linking), and finally by the development of copolymers of various nylon monomers.

This is today a highly dynamic field of research which can take many approaches. However, effort in much of this work can be optimized by advance consideration of the economic factors involved and by recognition of the many areas of exclusion which the great backlog of earlier investigations has delineated. Obviously, its effective planning is an undertaking well beyond the scope of the present examination.

Instead, the present article will seek to bring out some of the major considerations which must guide such planning, and it will report on some of the principal approaches to the development of new commercial nylons which are now current.

Goals of New Nylon Development

Advantages of the generic group of polyamide fibers may be summarized as follows: outstanding tensile strength and abrasion resistance as well as bending strength; high elasticity; small moisture absorption which results in ease of washing and quick drying characteristics; ability to form knife-edge creases by heat-setting; high dimensional stability of nylon fabrics; lightness of fabrics by reason of low specific weight.

Against this, the following disadvantages may be cited for polyamide fibers and fabrics made from them: high electrostatic loading which also favors soiling; moderate resistance against influence of light; "pilling" of fabrics made from spun yarns (a tendency which may, however, be minimized by changing the shape of the fiber cross-section); high elongation at low tensile stress, a characteristic which requires special attention during processing.

The development of new nylons is directed toward production of fibers which excel the present commercial grades in their inherent physical properties (melting point, water absorption, tenacity, etc.), in their processing characteristics (improved crease-resistance, bulk and crimp development in the fabric, etc.), and in their specific performance (non-flatspotting, antistatic and moisture regain properties). The approach involves three main lines of attack: (1) modification of the basic polymer structure, (2) physical modifications of existing nylon types, and (3) formation of mixed polymers and copolymers.

The broadest line of attack has been taken on the modification of the basic polymer structure. Here, variations may be made in molecular weight, in choice of monomer, and in extent of cross-linking (if any).

The importance of molecular weight is reflected, above all, in terms of tensile strength. To achieve the higher tenacities which can be obtained by use of polymers of high molecular weight, calls for monomer of very high purity. Against this, excessively high molecular weight causes difficulties in the spinning process. Thus, the presence of a small amount of polymer of low molecular weight is often desirable in the product; its removal by water extraction is practiced where this is called for by product specifications (in nylon-6). Typically, commercial nylon-6 has an average molecular weight of 16–22000, and nylon-66 is in the range 15–18000.

As a readily determined physical property, the dependence of softening point of polymer on molecular structure has probably been more extensively investigated than that of any other property. Here, it may be noted that the molecular weight has a significant influence only up to a point (which depends on the monomer structure). I.e., softening pont rises with molecular weight until it reaches a constant level beyond which further increase of molecular weight remains without effect.

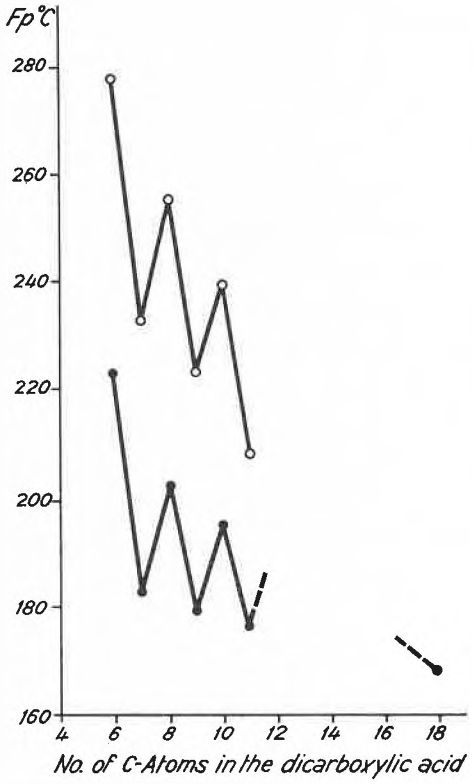

Fig. 1. Melting points of polyamides from diamines and dicarboxylic acids. ○—○ Tetramethylene diamine, ●—● Pentamethylene diamine

Against this, the structure of the monomer has a very pronounced effect on the polymer's melting point. Within each homologous series, the melting point gradually declines with increasing molecular weight of the monomer. However, as shown in Figures 1 and 2, the melting point for even-numbered $-CH_2-$ chains is higher than that of adjacent odd-numbered chains. The following general rules apply:

1. The melting point of polyamides decreases as the length of the hydrocarbon chains between amide groups rises.
2. The introduction of a side chain in lieu of an H-atom, in either a methyl or amido-group lowers the melting point.
3. Introduction of a phenylene ring into the chain of the polyamide's monomer molecule results in elevation of the melting point, particularly if the substituents are in *para*-position.

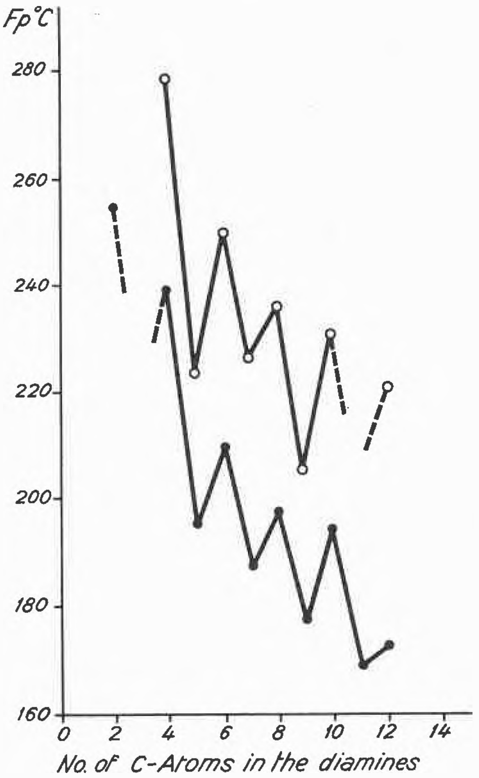

Fig. 2. Melting points of polyamides from diamines and dicarboxylic acids. ○—○ Adipic Acid, ●—● Sebacic Acid

The last-named effect of the phenylene group on the polymer's melting point is demonstrated in Figure 3.

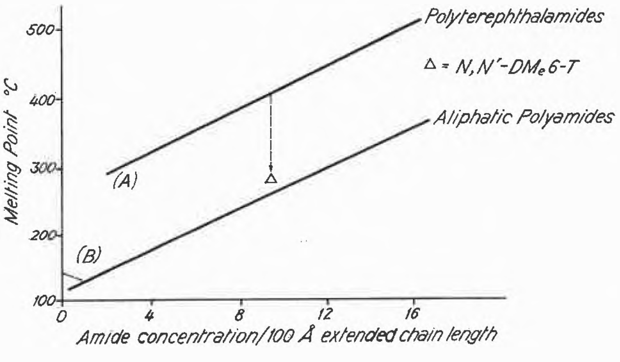

Fig. 3. Polyamide melting points v. amide concentration and chain stiffness

This phenomenon is utilized in Du Pont's recently commercialized "Nomex" high-temperature nylon. By contrast, Chemstrand's recently announced developmental high-temperature fiber has alternating *meta*- and *para*-substituted phenylene rings. *Meta*-substitution results in a melting point which is intermediate between that of straight-chain monomers on the one hand, and that of *para*-phenylene substituted monomers on the other. However, for this very reason, it presents less of a problem in the polymerization and spinning stages than does a *para*-phenylene substituted nylon.

Another property which is sharply affected by molecular structure is the maximum water absorption of the polymer, as demonstrated in Figure 4. This characteristic has been utilized in nylon-11 and -12, both of which are offered in Europe for applications (notably electrical) in which low water absorption is an essential property. In terms of fiber utilization, however, this characteristic has the drawback of resulting in more pronounced tendency to accumulate static electricity.

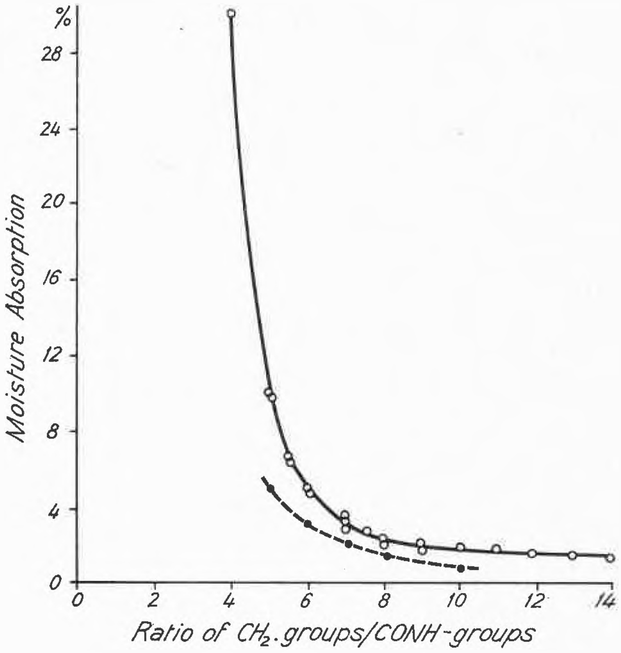

Fig. 4. Maximum water absorption of homopolyamides as function of the ratio of CH$_2$-groups to CONH-groups. ○—○ at 100% rel. humidity (20°C), ●– –● at 65%. H.R. (20°C)

As might be expected, not only polymer properties but also fiber properties are affected by the nature of the monomer. This effect is listed in Table 1 (3) for the commercially and potentially more important polyamides.

Production of Nylon Polymers

Essentially, the production of all nylon types involves one of the following reactions:

1. Polycondensation of dicarboxylic acids and diamines (e.g., in nylon-66).

Table 1. Properties of the Important Polyamides

Polymer	Polymer Properties					Fiber Properties			
	Specific Gravity	Melting Point °C	Molecular Weight Range	Moisture Regain %	Extractable with H_2O %	Tensile Strength Gm./Den.	Elongation to Break %	Wet Strength Gm./Den.	Wet Strength %
5-Nylon	1.13	240–250	14–16,000	4.1	5 –15	4.8	28	4.4	32
6-Nylon	1.12	210–215	16–22,000	3.6	5 –10	4.5	35	4.3	40
7-Nylon	1.10	225–230	16–25,000	2.9	1 – 3	4.2	35	4.0	33
8-Nylon	1.09	200–205	16–22,000	2.9	0.5– 2.5	4.2	38	4.1	38
9-Nylon	1.09	210–215	18–25,000	2.5	0.5– 1.5	4.2	40	4.1	40
11-Nylon	1.08	190–200	20–25,000	2.3	0.5– 1.2	3.8	38	3.7	38
12-Nylon	1.08	180–190	22,000	2.2	0.75	3.8	40	3.8	40
6,6-Nylon	1.13	250–260	14–18,000	3.4	0.5– 0.9	4.5	22	4.2	28
6,10-Nylon	1.10	190–195	16–22,000	2.6	0.5– 0.8	4.2	30	4.1	32

2. Polycondensation of ω-aminocarboxylic acids containing more than four CH_2-groups. This technique is employed in the manufacture of nylon-11 in France and the U.S.S.R.
3. Polycondensation of lactams containing more than six ring members. This is the approach in nylon-6 and -12.

These reactions open a vast field of possible syntheses, and many hundred different polyamides have been investigated. Not all are technically useful as fiber-forming linear polyamides, however, and the following principles apply:

1. Formation of useable, fiber-forming linear polyamides require the use of dicarboxylic acids which do not tend to internal ring formation at the conditions of reaction (e.g., succinic acid or glutaric acid are unsuitable).
2. The same limitation applied to the diamines, so that ethylene diamine or trimethylene diamine are similarly unsuitable.
3. Melting point and decomposition point of the polyamides may not be too close together since otherwise losses and discoloration will occur during melt spinning. A spread of at least 10–15°C is recommended between melting and decomposition points.

Techniques employed for the polymerization and spinning of nylons formed from lactams (such as nylon-6) differ significantly from those employed for the copolymer of diamines and dicarboxylic acids. Because this aspect also affects the relative economic attraction of different nylon types, it will here be briefly discussed.

A. Polycondensation of Lactams

The condensation polymerization of caprolactam is today normally carried out on a continuous basis. The reaction is carried out in concentrated (80–90%) aqueous solution at 250–280 °C, using 0.2 to 0.5% acetic acid as initiator (other acidic materials, including ε-aminocaproic acid or AH salt may also be used, in which case the initiator appears as part of the polymer).

Upon completion of the polymerization, nylon-6 polymer retains an equilibrium content of 5–10% monomer which must be reduced to 1.5% by washing with hot water before the polymer is melt-spun. Under the conditions of melt-spinning, however, the monomer content once again builds up to 5% by equilibration, so that the product fiber must once again be washed. It is, however, significant that the polymer melt containing 5% is thermally stable and can be kept at 250 °C for 16–24 hours without deterioration.

This high thermal stability makes caprolactam highly suitable for continuous polymerization-spinning processes. As we shall see, the lower thermal stability of nylon-66 above its melting point makes this material less suitable for continuous manufacturing processes. Thus nylon-6 staple is already being produced on a large scale by continuous polymerization followed by direct spinning of the melt, and the outlook for extensive application of this technique to production of nylon-6 yarns is good.

While hydrolytic polymerization of caprolactam is the conventional way to production of nylon-6 fiber, ionic polymerization of lactam in non-aqueous system offers good possibilities for monomer casting of polyamide plastics. In this technique, alkaline catalyst and activators (usually acylating agents) are added to essentially anhydrous caprolactam melts, and the mixture is pumped directly into a mold chamber where the castings harden in less than 30 minutes, with a residual monomer content of 2–3%. This technique achieves substantially higher molecular weight than is obtained by conventional hydrolytic production of nylon-6. The result is improved toughness, fatigue resistance and weathering behavior. Other properties (such as tensile strength, modulus, and dimensional stability) are improved by this technique which yields a more highly crystalline polymer than is obtained in hydrolytic polymerization.

Hydrolytic polymerization, similar to that described above for caprolactam, also serves in the polycondensation of the higher commercial lactams, i.e., in the production of nylon-7 to nylon-12 polymer chip. Differences are noted principally in the extent of monomer content at equilibrium. This decreases with increase in the monomer's ring size (e.g., monomer content of nylon-6 at equilibrium at 230 °C is 6%, while it is less than 1.5% in nylon-12).

Furthermore, there are sharp differences in reaction rate; polymerization of caprolactam is slower than that of caprolactam (nylon-8), but substantially more rapid than that of lauryl lactam (nylon-12). In the latter case, however, the slow reaction rate may be offset by operation at higher temperature because of the greater thermal stability of nylon-12 melt.

B. Polycondensation of Dicarboxylic Acids with Diamines

Here, the commercially important example is the production of nylon-66 from adipic acid and hexamethylene diamine. It is essential that the two co-monomers are in exact stoichiometric balance, since otherwise the polymerization chain is interrupted prematurely, i.e., the product will not reach the desired high molecular weight.

To achieve this needed stoichiometric balance, the co-monomers are fed to the polymerization reaction, not as such, but in the form of the AH-salt (i.e., the salt formed by neutralizing adipic acid with an equimolar quantity of hexamethylene diamine). In typical operation, this salt is produced by mixing a 50% solution of HMDA in methanol with an approximately equivalent quantity of adipic acid (as 20% solution in methanol). The exothermic reaction is carried out with careful temperature control.

AH-salt formed in the course of neutralization is relatively insoluble in methanol. It is therefore precipitated, upon cooling, in finely crystalline form and in a yield of approximately 95% of theory (the mother liquor must be reworked to avoid buildup of impurities which would harm the polymerization process). The salt is separated from the mother liquor by centrifuging, followed by methanol washing and final drying.

The same technique is applicable to the production of other salts of diamines and dicarboxylic acids which serve in nylon production, such as SH-salt, i.e., the product obtained from sebacic acid and HMDA as intermediate step in the manufacture of nylon 6/10.

AH salt is polycondensed in 60% aqueous solution in the presence of a chain regulator such as acetic or adipic acid. Concentration of the regulator (typically between 0.5 and 1 mole % based on AH salt) is controlled by the viscosity (a measure of molecular weight) which is desired in the product melt.

The polycondensation is carried out with careful exclusion of oxygen from the system. Typically, the reaction is allowed to take place in two reaction steps: (1) precondensation carried out at 220–230 °C for 1–2 hours, and at a pressure of 225–250 psig, corresponding to the vapor pressure of water at this temperature; (2) this is followed by polycondensation at 275 °C. While the batch is gradually raised to the polycondensation temperature, steam is carefully vented from the system so as to maintain an internal pressure below 250 psig.

Once the desired temperature (275 °C) has been reached, residual steam is bled from the system. To achieve this, the batch is either held at 275 °C and atmospheric pressure for about one hour or, more commonly, a vacuum is applied at this temperature until water has been removed to the point where the batch has the desired viscosity.

Unlike polycaprolactam, the nylon-66 polymer is quite susceptible to thermal deterioration; even relatively short retention of the polymer at 250 °C leads to degradation and foam formation. This makes it necessary to remove nylon-66 melt from the polymerizing autoclave almost immediately following formation, so that development of a continuous polycondensation process is fraught with difficulties; none is commercial so far. Instead, the reaction is carried out on a batch basis, the polymer is cooled and solidified, and the resulting chips are remelted immediately preceding the subsequent spinning operation.

Despite the described difficulties which are inherent in the development of a continuous polymerization and polymerization-spinning process for nylon-66, there is no lack of attempts to achieve this type of an operation. Thus, announcement has recently been made of a promising continuous process now in pilot-plant development by Imperial Chemical Industries. Key to the process is a design which minimizes polymer retention time at all high-temperature stages.

C. Polycondensation of ω-Aminocarboxylic Acids

This technique is doday of commercial or semi-commercial significance in the production of nylon-7 and -11. Inherently, it greatly widens the field of nylon types which can be produced.

For the polycondensation of aminocarboxylic acids which contain more than 5 CH_2-groups the method is straight-forward. The polycondensation can be carried out simply by heating slightly above the melting point of the system, with exclusion of air. Application of pressure is not necessary.

A high reaction velocity makes these aminocarboxylic acids suitable for continuous, low-pressure polycondensation. The resulting polymer is identical to that formed from the corresponding lactam. Thus, the product contains a small quantity of monomeric lactam, as determined by the equilibrium considerations outlined above.

The commercial polycondensation of 11-aminoundecanoic acid to nylon-11 polymer has been described by Genas (4). Here, an aqueous suspension of the monomer, catalyzed by phosphoric acid, is fed to a three-stage reaction column. In the first section, water is removed, the monomer is melted, and polycondensation begins. In the second part, the polycondensation is allowed to proceed to completion. In the third section of the reactor, the polymer is retained for some time in order to achieve a more uniform distribution of molecular weight. The resulting molten polymer is taken to an intermediate storage tank from which it is fed directly to the spinnerettes.

Potential of the New Nylons

Three approaches are available to modify the physical properties of nylons in response to a given need.

Physical modification of the formed fiber (either during or after the spinning process) can affect both strength and wearing characteristics. Drawing or stretching the spun fiber, above its glass-rubber transition temperature, to several times its original length enhances the degree of orientation and crystallinity of the polymer molecules. The result is substantial increase in tenacity and flexibility.

Aesthetics and performance characteristics (notably bending stiffness) of the fiber can be critically influenced by varying the cross-sectional shape of the fiber. Multifilament nylon yarns with multilobal filament cross-sections permit the weaving or knitting of fabrics with a dryer or warmer silk-like hand.

Adaptation in stress-strain characteristics by physical modification is widely practiced to make nylon compatible with such fibers as cotton. It is this control which has permitted the production of high-strength blends with cotton which contain up to 25% nylon. By contrast, blends produced with conventional nylon staple had shown a decrease in fabric strength and tear resistance.

A major thrust of development in nylon fibers is toward improved texturizing or bulking techniques. Here, a significant recent development has been the introduction of a nylon filament (Du Pont's "Cantrece") which permits bulking in the fabric during fabric finishing. This technique is in contrast to present methods in which the (textured) filament is bulked before the fabric is made.

Ability to post-bulk opens up significant possibilities in varying fabric bulk, cover and handle and may improve the economics of producing bulked fabrics. Initial application is expected in the production of tricots and hosiery, and good longer-range potential is also seen in wovens. The post-bulking technique in fabrics has already established its commercial value in the case of acrylic fibers where staple yarns are available which develop bulk or crimp during fabric finishing. "Cantrece" nylon extends this concept to filament fabrics.

This effect in "Cantrece" is achieved by incorporating into the yarn two different polymers in a bicomponent mixture. These two nylon polymers have different shrinkage characteristics upon application of dry heat or in boil-off so that, under these conditions, a spiral crimp develops which can be controlled by the fiber tension during treatment, by temperature during the bulking stage, and by proper selection of the polymers or copolymers in their fiber. TIPPETTS (2) points out that this bicomponent fiber makes it possible to tailor a wide array of new nylon yarns for hosiery, for knitted or for woven fabrics.

Chemical modification of existing nylons includes, above all, introduction of graft polymers and of cross-linked structures. Graft polymerization of ethylene oxide onto nylon-66 can, for example, achieve significant improvement in the fiber's flexibility as well as an increase in its hygroscopicity. A newer technique, radiation-induced grafting, permits introduction of vinyl monomers in side chain position of the nylon polymer.

Significantly, this type of grafting occurs manly in the amorphous areas of the polyamide substrate. Thus, properties which are determined chiefly by the polymer's crystalline areas—notably tenacity and stiffness—remain essentially unaffected. On the other hand, properties which depend chiefly on the amorphous areas, such as dyeability, moisture regain, etc. are greatly changed.

Sodium salts of acrylic acid grafts on nylon-66 have been shown (5) to provide a highly hydrophilic product which has high wet-crease recovery properties. The basis is thus given for a novel type of setting treatment on nylon which is different from and additive to heat treating. By contrast to ungrafted nylon, the calcium salts of acrylic acid grafts are infusible. As a result, the fiber melt temperature of such grafted polymers can be raised from 250°C to above 350°C, depending on graft level.

Cross-linking of nylon is Allied Chemical Co.'s approach to minimizing the flatspotting problem which has been a key obstacle to the use of nylon cord in original-equipment automobile tires.

Allied's method involves a short, vapor-phase exposure of nylon-6 fiber to isocyanates. The company claims that this not only reduces flatspotting but renders the fiber highly satisfactory for radial ply tires, where nylon's high extensibility has been a shortcoming in the past. Two or three pounds of toluene diisocyanate used to cross-link one hundred pounds of nylon-6 results in a reported 33% reduction in the flatspotting index. According to Allied, the cross-linking progress from the outside in, permitting diffusion control. When about one-fourth of the fiber cross-section has been cross-linked, a significant increase is realized in modulus. Further treatment produces little gain.

The above examples are merely meant to illustrate the very large range of possibilities which are opened by graft polymerization and cross-linking techniques in modifying nylons. This approach is still in its infancy; its potential is very considerable.

The most radical way to production of new nylons is *modification of the basic polymer structure.* In this area, a vast amount of research effort has been and continues to be expended. One may hardly expect a "new" nylon from this source. Instead, the key to commercialization is held by the economics of monomer production. At the present state of technology, the lowest-cost nylon raw materials are the C_6-monomers, i.e., adipic acid, hexamethylene diamine, and caprolactam which are, indeed, the raw materials for the only general-purpose polyamides, nylon-66 and nylon-6.

No development is now on the horizon which promises to provide an independent source of other nylon monomers at lower cost. And it should be borne in mind that the commercial introduction of a new fiber is accompanied by so many difficulties and obstacles, and by such high cost to both manufacturer and converter, that a marginal price advantage is not enough. This aspect is highlighted by the different marketing experiences with nylon-6 and nylon-66 in the U.S. and in Western Europe, as outlined earlier in this article.

The best present hope for new nylons is to fill speciality needs. Thus, nylon-12 has already carved a niche for itself (approximately ten million pounds/year) in Germany and France, and may soon reach commercialization in the U.S. Nylon-11 enjoys a small commercial position in France and U.S.S.R., as well as in Brazil and India (where a special raw materials position can be utilized). Chemical modifications containing phenylene groups (e.g., "Nomex") are becoming commercially significant in the U.S., as discussed. Nylons containing cycloparaffinic groups as well as nylon-7 (which is inherently superior to nylon-6) are in semi-commercial development. The use of a second type of nylon, to be blended with nylon-66 is indicated in the manufacture of "Cantrece" nylon.

Some of the basic rules governing the properties of homologous types of nylon, as well as the effect of introducing phenylene substituents, have been outlined above. It now appears in order to take a look at some of the individual specialty nylons which are today either commercial or are being considered for commercial introduction.

Nylon-3. Beta-lactams can be readily polymerized to form the corresponding substituted nylon-3. The ease of polymerization declines with increasing degree of substitution. Either hydrolytic polycondensation or anionic polymerization can yield polyamides of very high molecular weight (up to 500000) and, indeed, a nylon-3 fiber for textile purposes requires an average molecular weight of at least 200000. Significantly, the spun fiber is highly crystalline, even without drawing.

The raw material beta-lactam is obtained by the reaction of secondary or tertiary olefins with N-carbonylsulfamyl chloride, the latter being a condensation product of cyanogen chloride and sulfur trioxide. Though the polymerization step is relatively straight-forward, spinning the chip into filaments is rendered difficult by the high melting points and low solubilities of the polymers. Several of the substituted polymers are subject to decomposition at their melting point (around 300 °C). One process which has been explored on a developmental scale involves spinning from a methanol solution of calcium thiocyanates in which some of the nylon-3 polymers are fairly soluble.

The fibers are characterized by high melting point and excellent resistance against oxydative attack. Dyeing characteristics are similar to nylon-6, though the affinity for dyes is somewhat lower.

Nylon-4. Pyrrolidone is the raw material for nylon-4 types which have undergone a small amount of commercial development (e.g., by BASF and by General Aniline and Film). Pyrrolidone is synthesized by the condensation of formaldehyde with acetylene to form butyne diol which is converted, via butanediol-1.4, to ammonia to form pyrrolidone.

Anionic polymerization, catalyzed by alkali and promoted by acyl compounds, permits a reasonably satisfactory polymerization of pyrrolidone. On the other hand, the hydrolytic polycondensation of this monomer does not lead to a polymer suitable for fiber formation.

Because polypyrrolidone is almost quantitatively reverted to its monomer above 265 °C, melt spinning can be achieved only by techniques in which the polymer's high-temperature retention time is minimal. Nevertheless, melt spinning is preferable to solution spinning because filaments of higher tenacity are formed. The resulting nylon-4 is not, however, superior to nylon-6 in any significant aspect except melting point (which can be raised by other means such as introduction of phenylene groups). Moreover, nylon-4 exhibits such high water absorption that oxidative degradation and soiling can be expected to be serious obstacles to satisfactory use.

Thus, no offsetting advantage is seen in the performance characteristics of nylon-4 which might justify the relatively high cost of its monomer and the technical difficulties in producing and spinning the polymer.

Nylon-7. Typical melting point of this polymer is 220 °C (v. 208 °C for nylon-6) and moisture absorption at 20 °C and 65% R.H. is 2.6%, compared with 4.7% for nylon-6. Nylon-7 thus has inherent advantages over nylon-6 which have justified its careful consideration as a fiber of commercial potential.

Again, the material's future depends on monomer economics. Broadly speaking, its physical properties are intermediate between those of nylon-6 and nylon-66. Because of its higher wet modulus at 40–60 °C, however, the wash-and-wear properties of nylon-7 are expected to be superior to those of either nylon-6 or -66.

Two processes for the manufacture of the monomer are of potential interest: (1) telomerization of ethylene on a carbon tetrachloride substrate, and (2) synthesis of 7-amino-heptanoic acid from cyclohexane via ε-caprolactone.

Of the two processes, the first-named is today commercial in the U.S.S.R. Three key steps are involved: telomerization of ethylene in the presence of carbon tetrachloride to form 1-chloro-7-trichloro-heptane; this is followed by hydrolysis to the ω-chlorocarboxylic acid, and finally by ammonolysis to ω-amino-undecanoic acid.

Of the three conversions, the first step (telomerization) is the key development. Azobisisopropyl cyanide serves as reaction initiator. Product distribution can be varied over wide limits by adjustment of operating pressure and ethylene/carbon tetrachloride feed ratio. In any event, substantial amounts of homologous aminocarboxylic acids are formed as co-products, and their effective utilization (e.g., for production of nylon-9 and nylon-11) is of crucial influence on the economics of the process.

Conversion of the tetrachloroalkanes to the corresponding aminocarboxylic acids is relatively simple. The first conversion involves reaction with concentrated sulfuric acid to yield ω-chlorocarboxylic acid which is then treated with aqueous ammonia at 150 °C to form the aminocarboxylic acid in 85–90% yield.

An alternative synthesis for the manufacture of 7-amino-heptanoic acid has been developed by Union Carbide Corp. The method involves production of caprolactone by the peracetic acid oxidation of cyclohexanone. The lactone is reacted with HCl in the presence of zinc chloride to form 6-chloro-hexanoic acid and this is built up to 6-cyano-hexanoic acid by reaction with sodium cyanide. The ester of this acid is finally hydrogenated to yield the corresponding ester of 7-amino-heptanoic acid.

The ester's polymerization properties are unsatisfactory. However, hydrolysis with water at 90–100 °C results in a predominantly monomeric product which can be readily subjected to hydrolytic condensation to achieve a fiber-grade polymer of molecular weight between 15000 and 30000. In inert atmosphere, the polymer is thermally stable above its melting point (225 °C) up to approximately 300 °C, so that melt spinning is readily accomplished. Unlike nylon-6, nylon-7 fiber contains, at equilibrium, only a small concentration (approximately 1.5%) of monomer and other extractibles, so that extraction is unnecessary, either prior to spinning or subsequent to it.

Nylon-8. No particular significance is attached to this polyamide. It can be produced from capryl lactam which, in turn, is synthesized from cyclooctane. This cyclic hydrocarbon is obtained by the dimerization of butadiene to cyclooctadiene which is then hydrogenated. (An alternative synthesis of cyclooctane leads from acetylene via cyclooctatetraene.) Conversion of cyclooctane to capryl lactam follows the techniques which are well established for caprolactam manufacture, and the related syntheses employed in the production of lauryl lactam which will be discussed below in connection with nylon-12.

Nylon-9. If any significance attaches to this fiber, it is only in conjunction with the production of nylon-7 and -11 since the telomerization reaction outlined above yields inevitably significant amounts of aminopelargonic acid (9-aminononanoic acid), the monomer for nylon-9. It is noteworthy that presence of less than 5% aminopelargonic acid in nylon-7 polymers has no significant effect on fiber properties. However, in common with other mixed and co-polymers among polyamides, C_9–C_7 polyamides exhibit a melting point curve which passes through a minimum. In the case of C_{7-9} polyamides, this minimum, observed at an aminopelargonic acid content of 60%, is 155 °C.

Nylon-9 polymers, readily produced by hydrolytic polycondensation, are quite stable in the molten state so that melt spinning is a feasible technique. The fiber is less hygroscopic than nylon-7; its hydrophobic character is, in fact, its best claim to a market position.

Nylon-11. This specialty fiber was developed by Organico (France) in collaboration with Italy's Snia Viscosa. In Organico's operation, the raw material is castor oil, and this is also the starting material in Brazil's production of nylon-11. By contrast, Russia's nylon-11 fiber is obtained from ethylene and carbon tetrachloride using a telomerization process akin to that described for the monomer of nylon-7. A third route in which undecanolactam is produced from dodecane is still in the developmental stage.

As an apparel fabric, nylon-11 is reported to have a softer hand than nylon-66. Furthermore, because of its hydrophilic character, it dries more readily than C_6-nylons, and therefore exhibits excellent wash-and-wear performance. Other advantages include good chemical resistance, low density, and excellent electrical properties, even at high relative humidity. Thus, the material is finding use in a variety of electrical and chemical service functions. It is today available both as simple and as stretch yarn.

The required monomer is 11-amino undecanoic acid. Its synthesis from ethylene and carbon tetrachloride follows the lines already indicated for the monomer of nylon-7. Its manufacture from castor oil, as practiced by Organico, may be briefly outlined.

Basically, this synthesis consists of a sequence of four reaction steps:

a) Castor oil consists of the triglycerides of ricinoleic acid together with a lesser quantity (10–20%) of other fatty acids. This material is transesterified with methanol to form methyl ricinoleate. The reason for this transesterification is the improved yield of undecylenic acid which can be obtained in step (b) when compared with a similar splitting of the triglyceride.
b) The methyl ester of ricinoleic acid is converted to a mixture of methyl undecylenate and heptanal by vapor phase splitting in the presence of superheated steam. At this stage, too, the methyl ester is hydrolized to undecylenic acid.
c) In a significant application of anti-Markownikoff addition of HBr to an olefin, undecylenic acid is converted to 11-bromoundecanoic acid. This reaction is carried out in countercurrent flow between the reactants at 0–30 °C, in the presence of air.
d) Bromoundecanoic acid is reacted with aqueous ammonia at 20 °C to yield 11-aminoundecanoic acid, the raw material for nylon-11.

Overall, approximately 3 pounds castor oil is required per pound nylon-11. The process is subject to wide fluctuation in raw materials price.

Nylon-12. Among aliphatic homopolyamides, this specialty nylon has attracted particularly extensive development work in recent years. As previously mentioned, the product is commercial in France and Germany, and may soon be commercial in the United States as well.

As a fiber, the principal advantages of nylon-12 over other commercial nylons are its low moisture absorption and its good dielectric properties. However, the product is inherently expensive and its use will be limited to specialty products.

Perhaps greater significance, though, attaches to the use of nylon-12 for specialty plastics and films. As plastic, the material is superior to nylon-6 because of its ease of fabrication and better dimensional stability. As concerns use of film, especially for food packaging (where authorized), nylon-12 has the great advantage over nylon-6 that there is almost no reversion to the monomeric or oligomeric form.

Raw material for nylon-12 is lauryl lactam. A number of potentially interesting syntheses for this material are possible; all start from butadiene-derived 1,5,9-cyclododecatriene (6). Particular interest attaches to the syntheses via cyclododecanone and its oxime, and via Oxo conversion of cyclododecene to cyclododecyl carbinol which can be oxidized to the corresponding carboxylic acid and finally converted to lauryl lactam according to the process developed by Snia Viscosa for caprolactam manufacture.

Miscellaneous Nylons. The effect on melting point of introducing aromatic rings into the molecular structure of polyamides is shown in Figure 3. This is the approach chosen by Du Pont in its high-temperature "Nomex" (formerly HT-1) nylon.

Use of metaxylene diadipamide (produced from metaxylene diamine and adipic acid) is commercial in Japan. Evaluations by Goodyear suggest that this type of nylon is second only to polyester fibers in its potential attractiveness in tire cord construction. However, this evaluation assumed a price of MXDA which can only be achieved in very large-volume production. More recent work by CELANESE (7) indicates that MXDA-type nylon is particularly sensitive to heat and moisture, and that it is therefore barred from a large range of textile applications.

Instead, CELANESE has turned to nylon-6T, a copolymer of hexamethylene diamine and terephthalic acid. As already noted, *para*-substitution of the benzene ring results in very high melting points. In the present instance, the melting point is reported at 370 °C—too high to permit melt spinning. Accordingly, it is necessary to spin this polymer by a wet process using concentrated sulfuric acid. Polymerization, too, may be expected to call for special techniques.

Structurally, this polymer combines aspects of nylon with those of polyester fibers. This intermediate position is also reflected in the resulting polyamide's physical properties which are intermediate between those of nylon-66 and polyesters. Thus, nylon-6T reportedly exhibits the density, moisture regain, abrasion resistance and elastic behavior of nylon, while its tensile modulus more closely resembles polyesters. The fiber has outstanding ability to resist stretch and very high work recovery at high temperature. Flat-spotting behavior is about the same as that of polyesters.

Chemstrand's recently announced developmental high-temperature nylon goes a step further in using aromatic substitution both in the diamine and the dibasic acid which make up the polymer. In this instance, ordered polymers are obtained by starting with a symmetrical diamine in which built-in amide linkages predetermine the order when reacted with diacid chlorides to yield alternating arrangements. The fibers thus contain benzamide structures and they have four phenylene rings in the repeating unit. Melting points or decomposition temperatures range from 410 °C to 555 °C. These high values are attributed to the regularity of the units in the chain. By contrast, a random polymer of like components would have a softening point of 300 °C and a clear melting point of 350 °C. Chemstrand's ordered polyamides show very high resistance to atmospheric degradation, even at 300 °C.

Introduction of the cyclohexane ring into the polyamide structure has been investigated by Tennessee Eastman Co. (8). The polyamides of *trans*-1.4-cyclohexane bis (methylamine) were found to have higher melting points than the analogous polyamides of *p*-xylene-α,α'-diamine. Polyamides of the *cis*-isomer of cyclohexane bis (methylamine) melted below those of the *trans*-isomer.

Other nylons which have been explored on a developments scale as potential fiber-forming materials include the copolyamides of adipic and isocinchomeronic acids with HMDA, polyoxamides (from oxylic esters and diamines), copolymers of caprolactam and aminotriazole, and others. Actually, the list of nylons which have been produced in the laboratory, following the general polycondensation techniques outlined above, has reached book-size proportions. In it, there is a large number of polyamides which have the technical suitability for development of successful fibers. The limitation barring their actual development is economic, due principally to less favorable monomer economics when compared with the raw materials for nylon-6 and nylon-66.

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